High Performance Oxide-Dispersion-Strengthened Tubes for Production of Ethylene and Other Industrial Chemicals

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Program Objective

- Develop a creep-resistant, coking-resistant oxide-dispersion-strengthened (ODS) tubing for ethylene pyrolysis and steam methane reforming.
- Program seeks to:
  - Develop an ODS Alloy 803 with creep strength comparable to INCOLOY® MA956
  - Produce co-extruded ODS Alloy 803/INCOLOY® MA956 tubing
  - Demonstrate that this tubing is viable for industrial service
- Expected to permit an increase of 65°C in tube operating temperature or a doubling of time between decoking cycles.

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Project Summary

Lead Organization: Institute of Materials Processing
Michigan Technological University
Houghton, MI 49931

Principal Investigator: Dr. Marvin G. McKimpson
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Project Partner: Special Metals Corporation—Huntington WV
Providing In-kind labor, materials and testing
Gaylord Smith / (304) 526-5735 (phone)

Performance Period: 9/30/2001 – 9/29/2008 (Currently in FY 2)

Projected Funding: ~$230K per year ($1.6 Million total)

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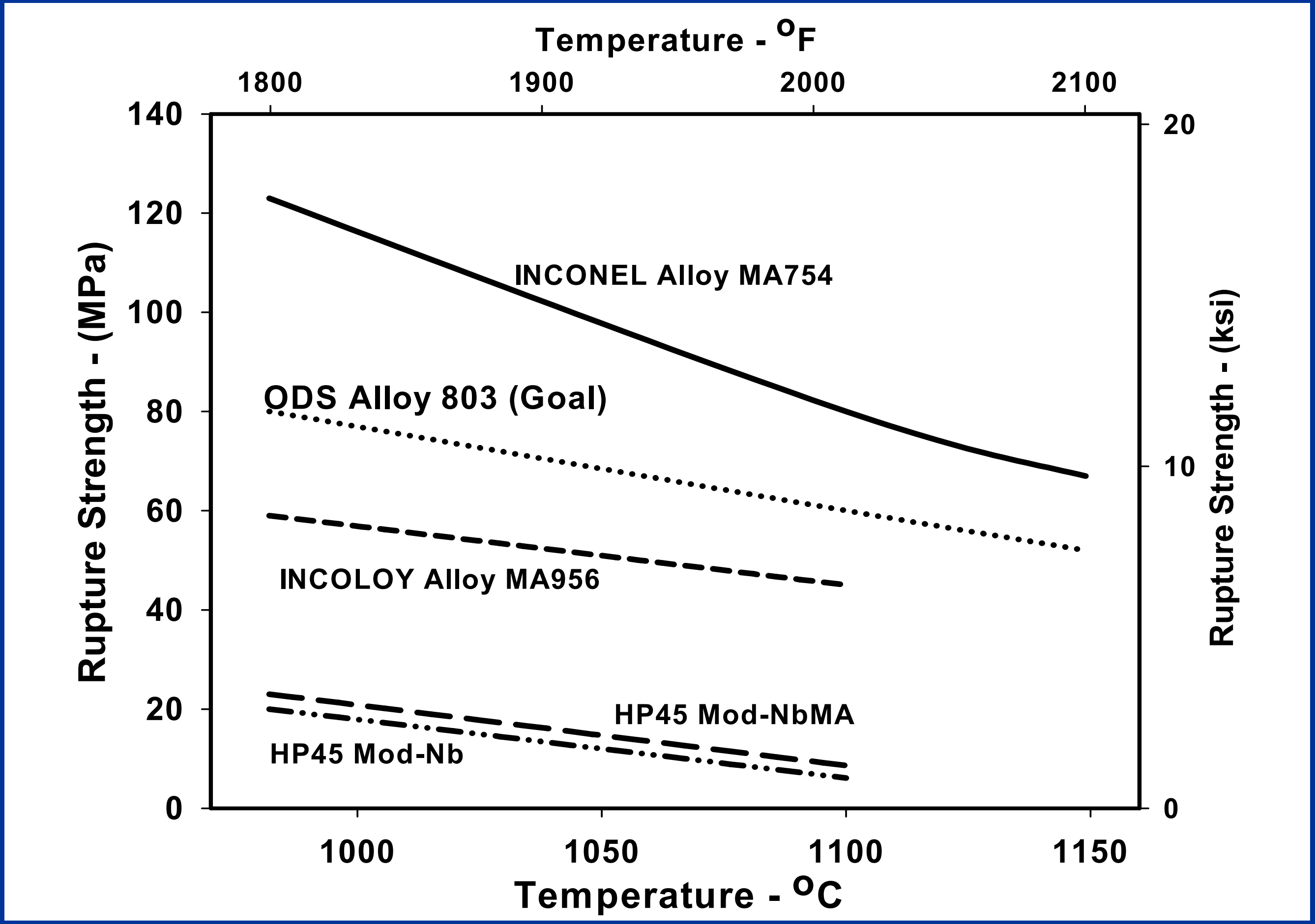
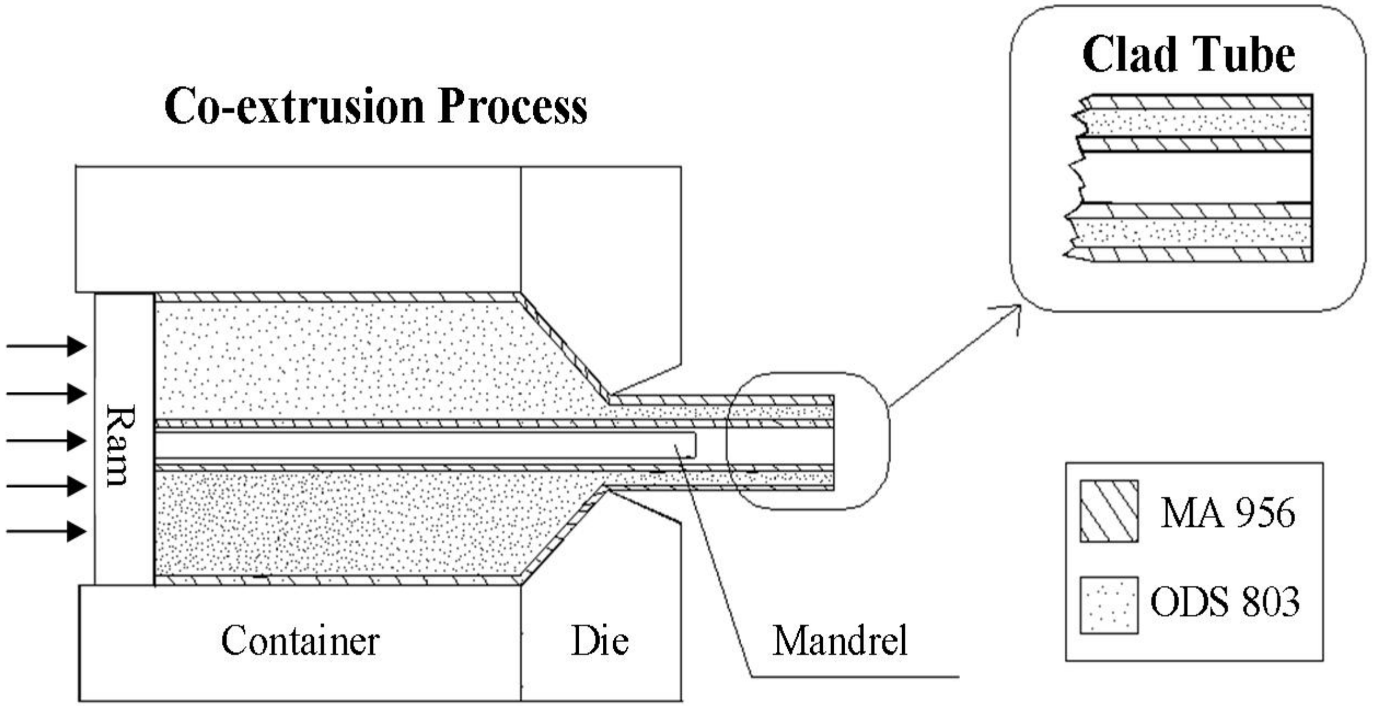
ODS Alloy 803 Goal



Tubing Concept



- MA 956 provides coking resistance on the tube ID and higher melting temperature material on the tube OD.
- ODS Alloy 803 provides greater fabricability, weldability and creep resistance in the tube core.

Ethylene Production

- Ethylene (C_2H_2) produced by pyrolysis of hydrocarbons
- Preheated hydrocarbons + steam injected into radiant coils and separated into ethylene and co-products.
- Maximum production of ethylene requires:
  - Low operating pressures (inlet pressures typically 370-640 kPa)
  - High tube wall temperatures (typically up to 1040-1120^{o}C)
  - Low residence time (typically 0.15-0.5 s)
- Tube metallurgy currently limits reactor performance
- Similar technology used for methanol and hydrogen

Radiant Coil Materials Issues

Coils experience some of most severe operating conditions for metals in the process industries

- High temperature creep
- Coking
- Carburization
- Oxidation and Erosion
- Field Repairability/Replacement

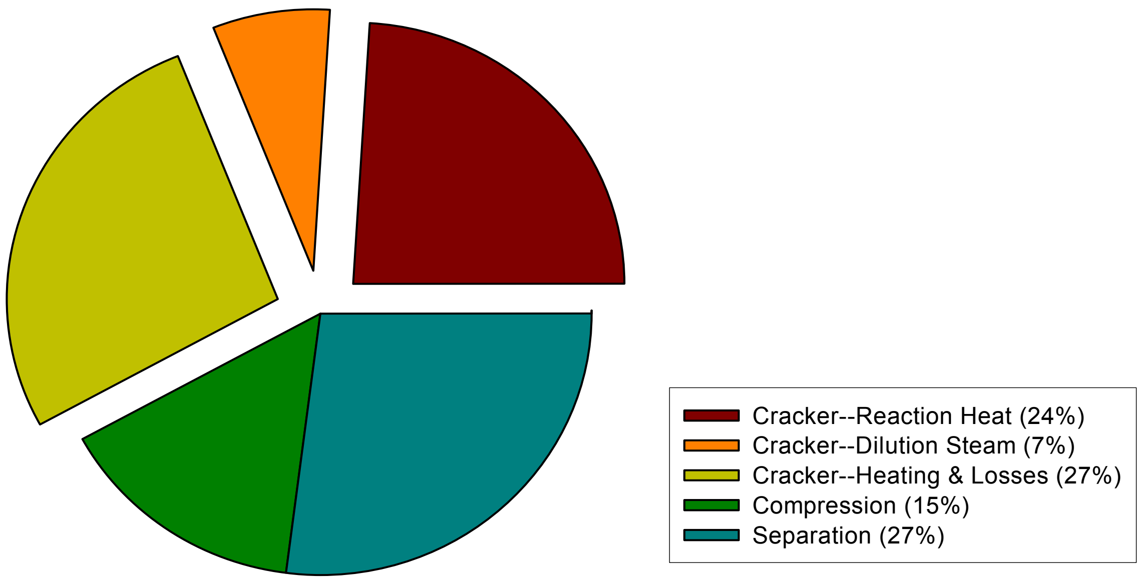
Current and Competing Technologies

- Current Technology
  - Cast HP Mod-Nb (and others) + Sulfur additions
  - Require periodic de-coking (~$9 million/yr/facility) and replacement every 3-5 years (~$1 million/replacement)
  - Limited capability for producing small-diameter tubes
- Competing Technologies
  - Several coating technologies, including in-situ Mn-Cr Spinel (Nova Chemical) and deposited alumina coatings
  - Alternate alloys, including intermetallics and higher-Cr materials (e.g. 35/45)
  - Most focused more toward reducing coking than increasing maximum tube wall temperatures

Technology Benefits

- Higher-temperature, fouling-resistant materials are a cross-cutting need for many Industries of the Future
- Co-extruded tubes targeted for:
  - Ethylene pyrolysis (Chemical and Petroleum Industries)
  - Steam methane reforming
    - Methanol production (Chemical Industry)
    - Hydrogen (Agricultural Industry—Ammonia-based fertilizers)
- ODS Alloy 803 also potentially useful as a heat-resistant material for fixtures, tooling and components (Process Heating, Glass, Steel & Metal Casting Industries)

Energy Usage for Ethylene Production



Domestic production of ethylene requires about 26 GJ/tonne (excluding feedstock). Note that 58% of this energy is consumed in the pyrolysis reactor.

(Data from E. Worrell et. al., *Energy Use and Energy Intensity in the U.S. Chemical Industry*, LBNL-44314, Lawrence Berkeley National Laboratory. April 2000. p. 16. Corrected for arithmetic error on Table 15)

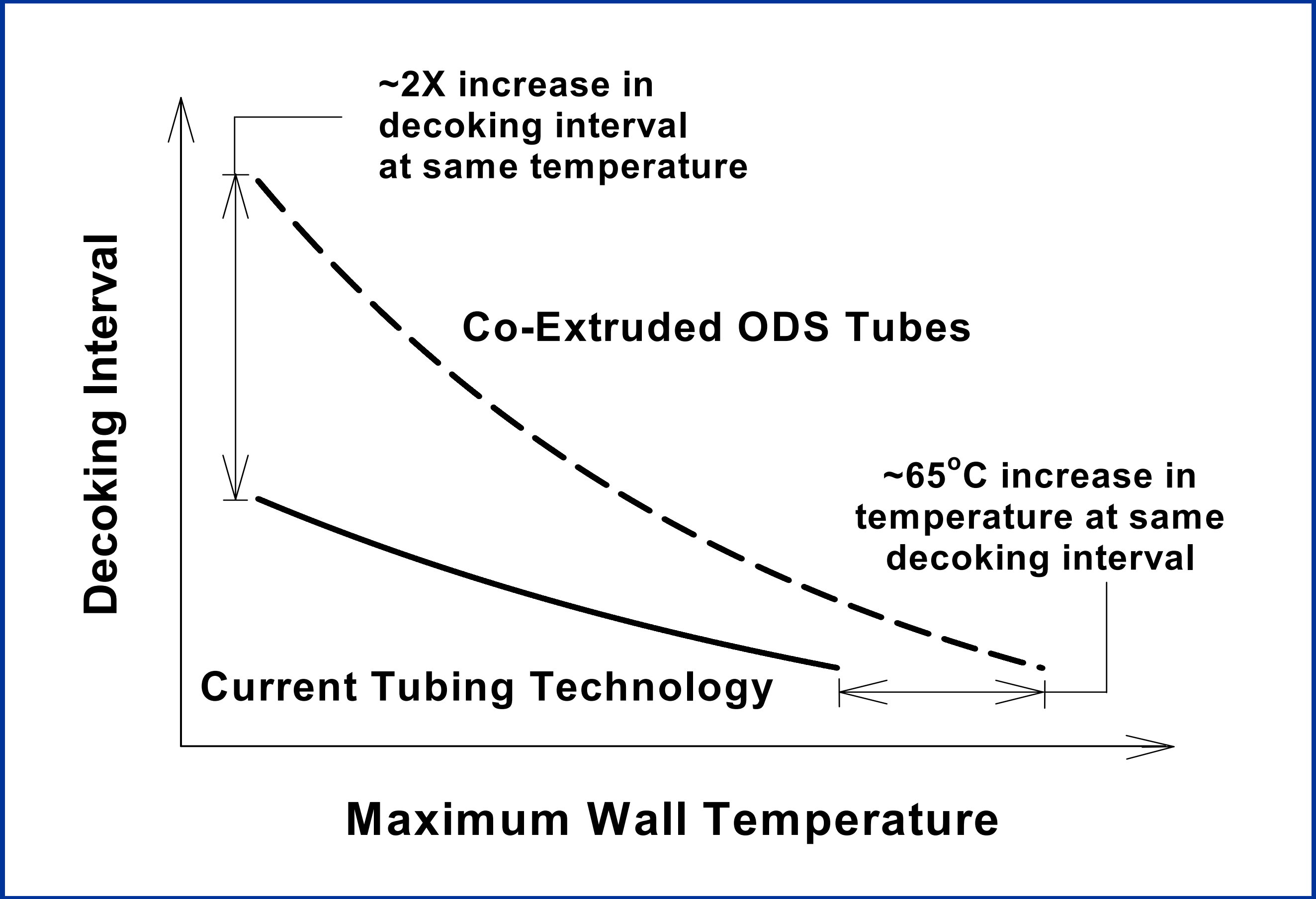
Pyrolysis Furnace Tubes

- Co-extruded ODS tubes will allow higher tube wall temperatures and/or thinner tube walls:
  - Core and cladding have higher creep strength than current alloys
  - Cladding provides improved environmental resistance against coking and carburization
  - ODS Alloy 803 core provides improved ductility and weldability
- Greatest energy and economic benefits likely to accrue from shorter hydrocarbon residence times—and increased productivity—in reactor furnaces

Energy and Economic Savings

- Projected energy savings of up to 25% for ethylene production
  - Maximum tube wall temperature increase by up to 65^{o}C
  - Reactor productivity increase by 35%
  - Energy savings due to:
    - Decreased coking
    - Increased conversion efficiency,
    - Improved heat transfer across thinner-walled tubes,
    - Higher reactor throughput
- Actual energy savings will depend on hydrocarbon feedstock, furnace design and operating parameters

Benefits of Co-extruded Tubes for Pyrolysis Furnaces (Schematic)



Composition of Selected Alloys

Alloy	Fe	Ni	Cr	Al	Ti	Si	C	Y_2O_3	Other
Incoloy® MA956	74.0	-	20.0	4.5	0.5	-	0.05	0.5	-
Incoloy® Alloy 803	36.0	35.0	27.0	0.4	0.4	0.5	0.08	-	0.8Mn
ODS Alloy 803	36.0	37.0	26.0	0.3	0.3	0.8	0.08	0.2	0.8 Mn
Inconel® Alloy 754	1.0	78.0	20.0	0.3	0.5	-	0.05	0.5	-
HK 40	53.0	20.0	25.0	-	-	1.8	0.45		-
HP Mod-Nb	37.0	35.0	25.0	-	-	1.8	0.45	-	1.0 Nb
HP Mod-Nb MA	37.0	35.0	25.0	-	-	1.8	0.45	-	1.0Nb, trace Ti, Zr and/or Rare Earths
35/45	16.0	45.0	35.0	-	-	1.8	0.45	-	1.5Nb, trace Ti, Zr and/or Rare Earths

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Technical Activities

- Task 1—ODS Alloy 803 Development (Completed)
- Task 2—Co-Extrusion Process Development
  - Flow stress development (FY 2)
  - Extrusion simulation—DEFORM™ (FY 2 +)
  - Co-extrusion and recrystallization studies (FY 2-3)
  - Clad tubing characterization (metallographic, mechanical and environmental testing) (FY 2-4)
  - Commercialization assessment (FY 2-4)
- Task 3—Pilot-Scale Demonstration
  - Development of appropriate industrial partnerships (FY 2-4)
  - Applications engineering of test components (FY 5)
  - Pilot-scale testing and evaluation (FY 6-7)

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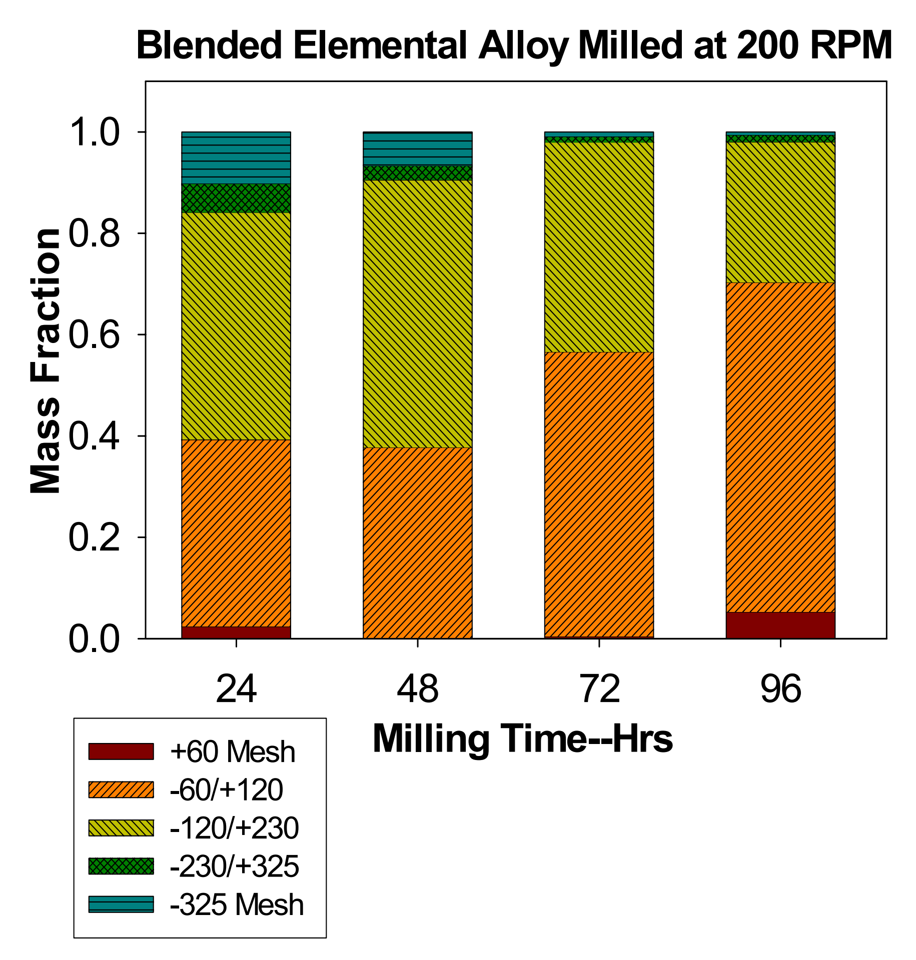
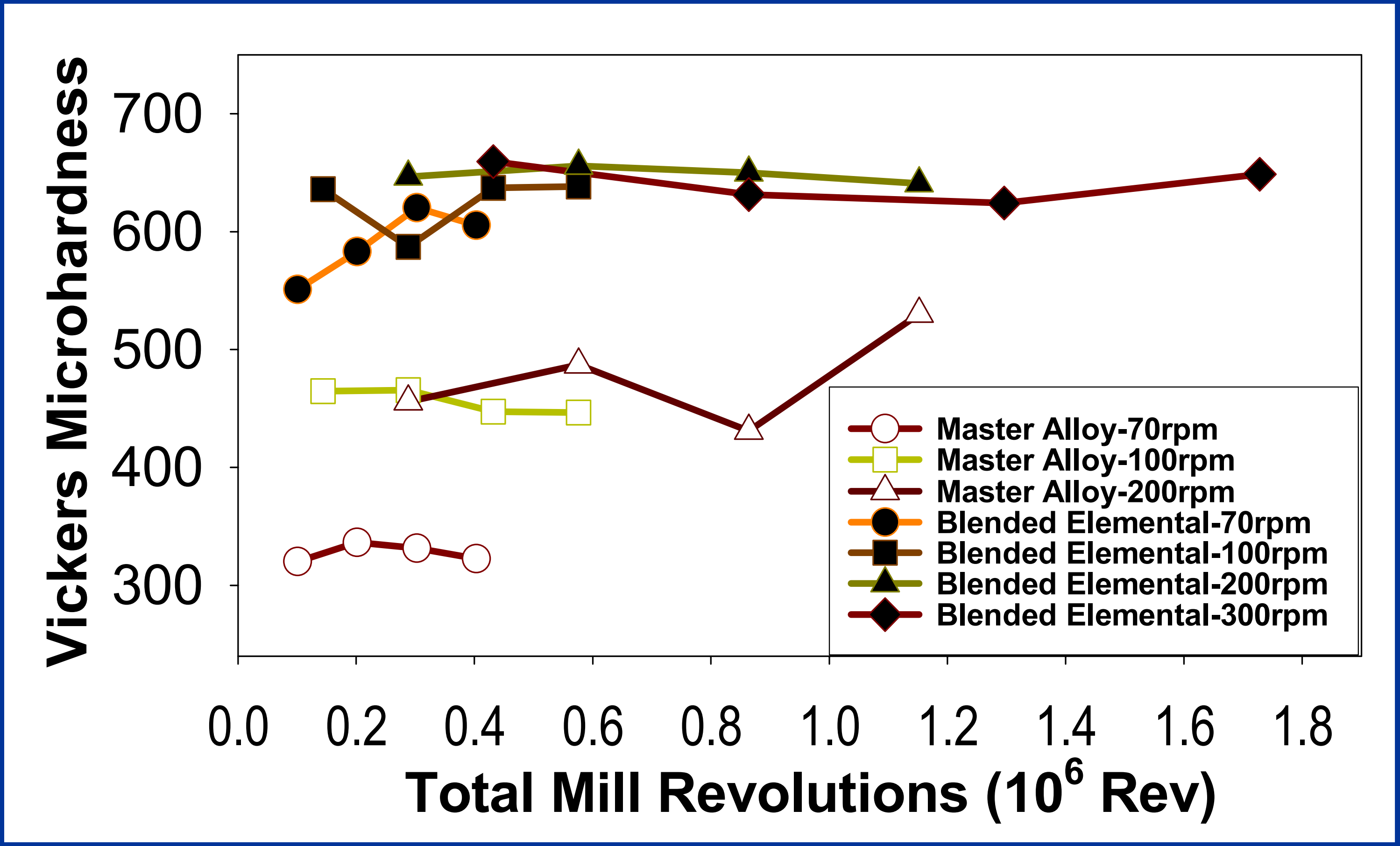
Task 1 — Milling Process Development

- Optimization studies completed
  - Parameters evaluated:
    - Speed—70 to 300 rpm
    - Time—0 to 96 hrs
    - Powders—Blended & Prealloyed
  - Characterized by:
    - Morphology
    - Microhardness
    - Particle size



Effect of Total Milling Revolutions on the Microhardness of Milled Powders



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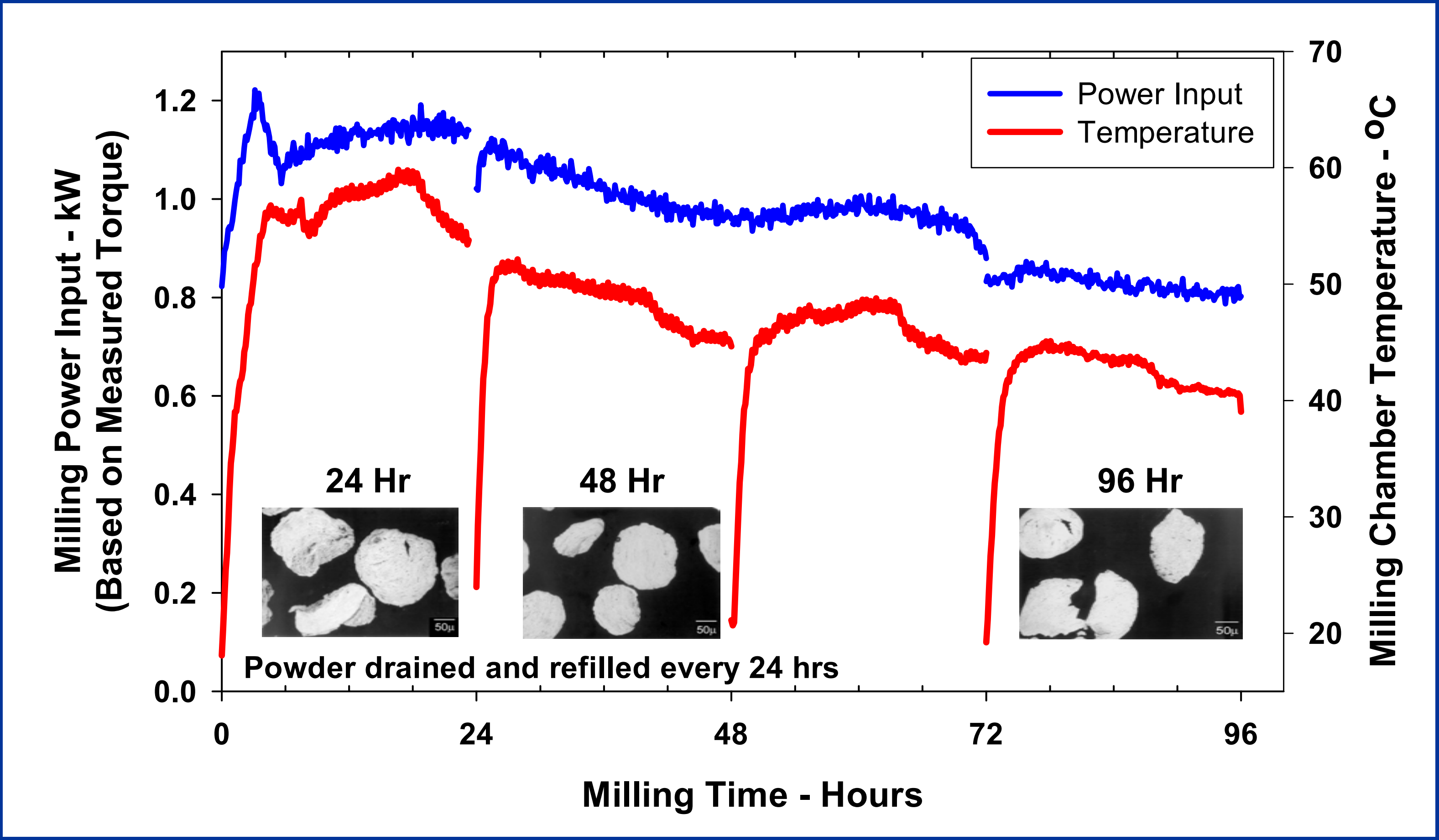
Representative Powder Milling Data



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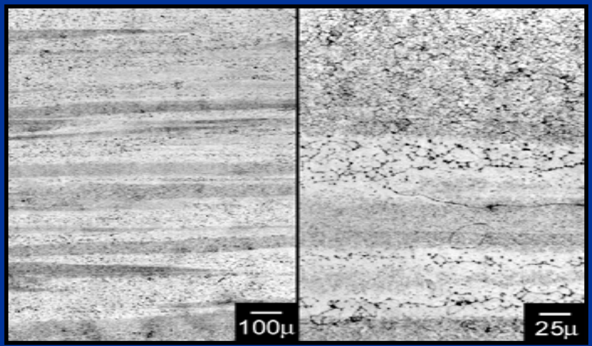
Task 1 — Extrusion Studies

- Billet Fabrication
- Recrystallization (1300^{o}C)
- Mechanical Properties (Recrystallized)
  - Yield strength—212-244 MPa (30.7-35.4 ksi)
  - Tensile strength—552-585 MPa (80-84.9 ksi)
  - Elongation—17.5-21.3%



ODS Alloy 803 microstructure after recrystallization

As-extruded ODS Alloy 803

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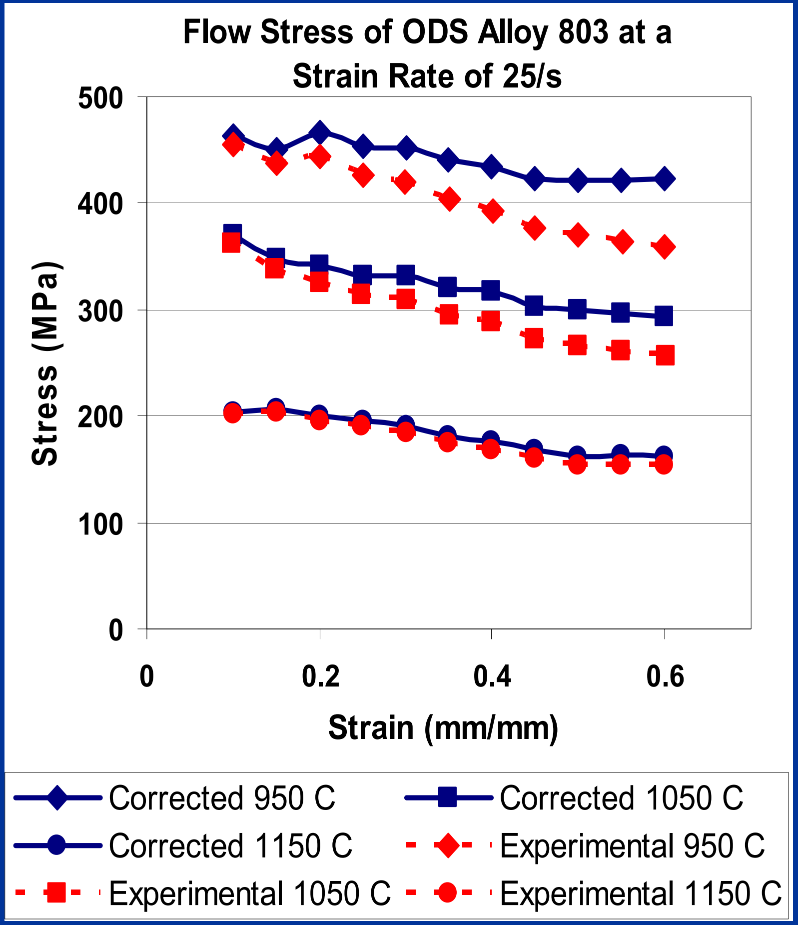
Current Activities

- Co-extrusion Development
- DEFORM™ Modeling
- Process Costing
- Additional Partners

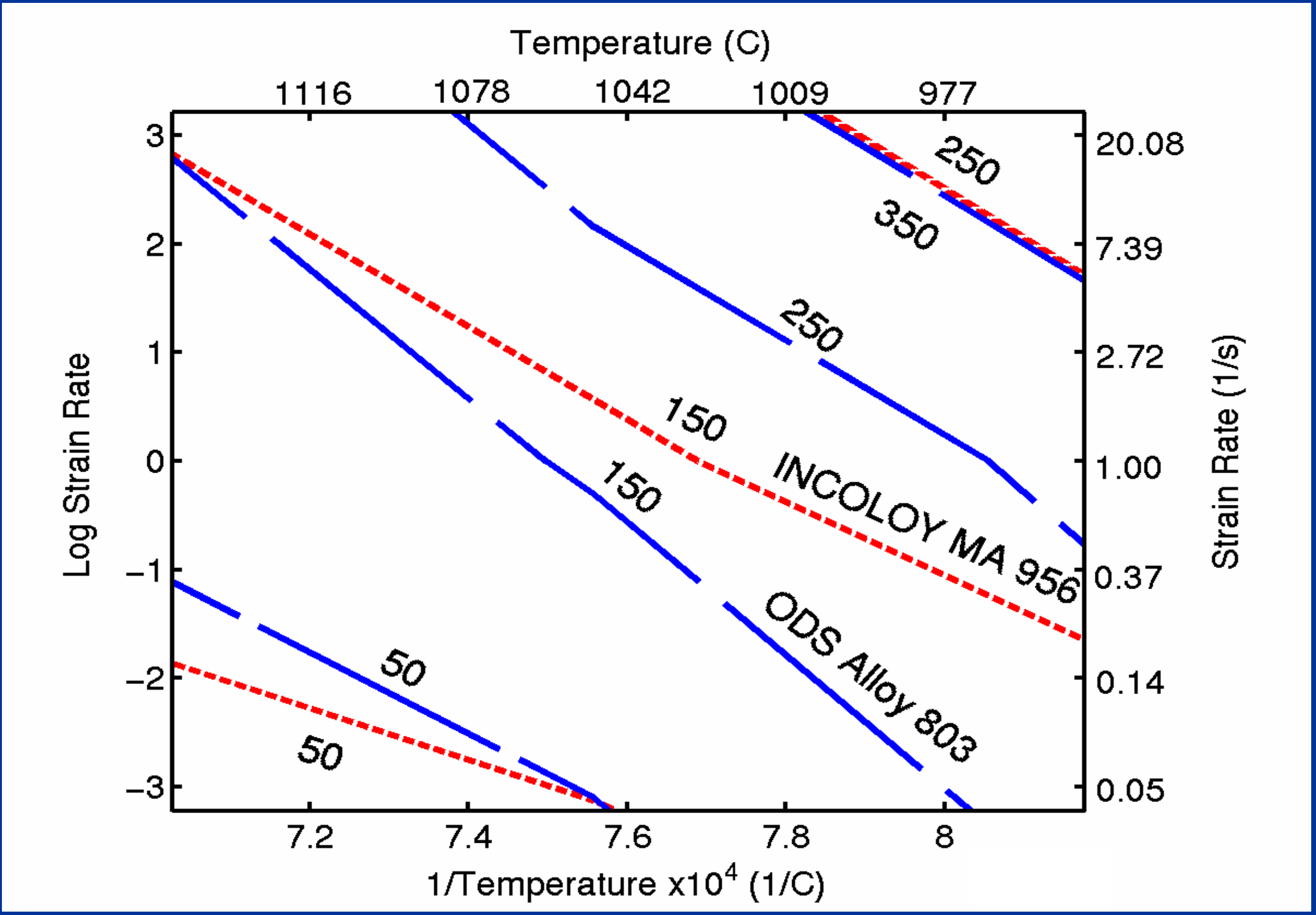
Canned ODS Alloy 803 powder ready for direct powder co-extrusion

Flow Stress Data

- **As-extruded INCOLOY® MA956 and ODS Alloy 803**
  - Hot Compression
  - 950, 1050 and 1150°C
  - 0.04, 1 and 25/s strain rate



Flow Stress (MPa) of INCOLOY® MA956 and ODS Alloy 803 at Strain=0.6



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Finite Element Simulation

- DEFORM™ is being used to model direct powder co-extrusion of the clad tubing
- Work includes:
  - Compile needed material/process input data
  - Verify initial clad tubing simulations
  - Perform sensitivity analyses
  - Use DEFORM™ output to asses:
    - Microstructure / deformation correlations
    - Process sensitivity
    - Process window

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Process Costing for ODS Tubing

Process Flow Diagram

Raw Material

Ni (37 wt%)
Fe (36 wt%)
Cr (27wt%)
Others (1 wt%)

↓

Ball Mill

↓

Direct Powder Extrusion

↓

Ship

Initial Assumptions

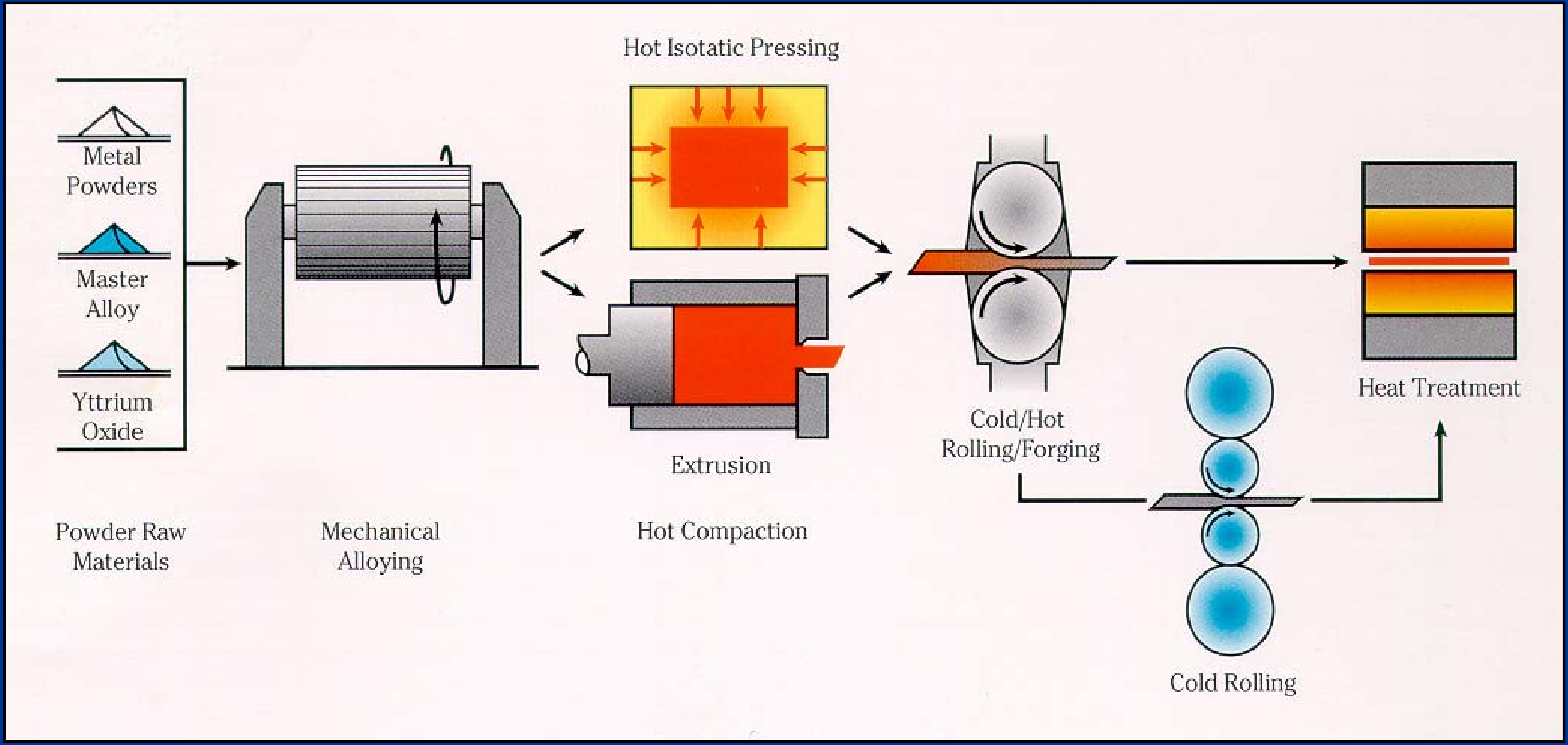
- **Initial production volume: 455 tonnes/year**
- **Tube dimensions: 63.5mm OD x 50.8mm ID x 12.2m Long**
- **Extrusion force— <53 MN**
- **Avg. raw material cost: $12.33 per kilogram (Includes MA956)**
- **Number of Ball Mills—4**
- **Required annealing time—1 hr**

Other processes include: screening, canning, machining, pickling and heat treatment.

Future Activities—Next 12 Months

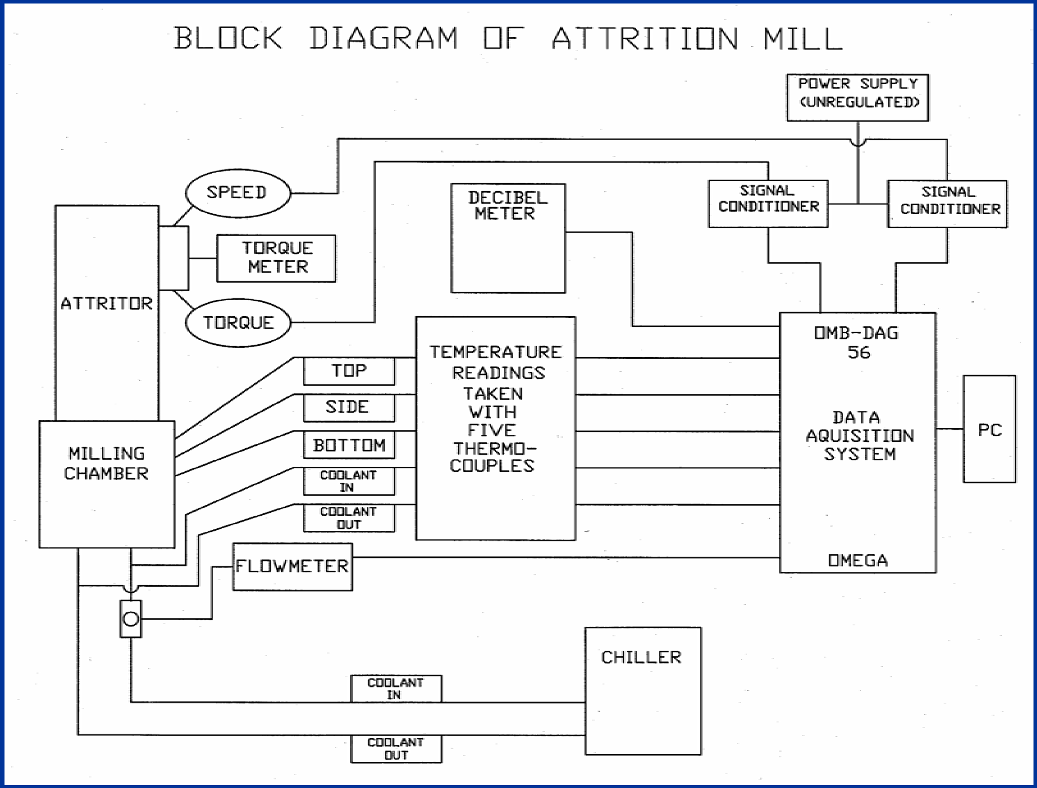
- Production/assessment of co-extruded tubes
- Completion of DEFORM™ modeling
- Mechanical and environmental testing of tubing
  - Ambient and elevated temperature tensile
  - Creep rupture (Special Metals)
  - Oxidation and carburization (Special Metals)
  - Coking (Planning for future tests)
- Completion of process costing study
- Strengthening of industrial interactions

Mechanical Alloying



"Oxide Dispersion Strengthened Alloys", Special Metals Corp.

1-S Data Collection System



ODS Alloy 803 Powder Development

24 hrs

Attrition milled ODS Alloy 803 powder

72 hrs

ODS Alloy 803 ready to be HIP'ped

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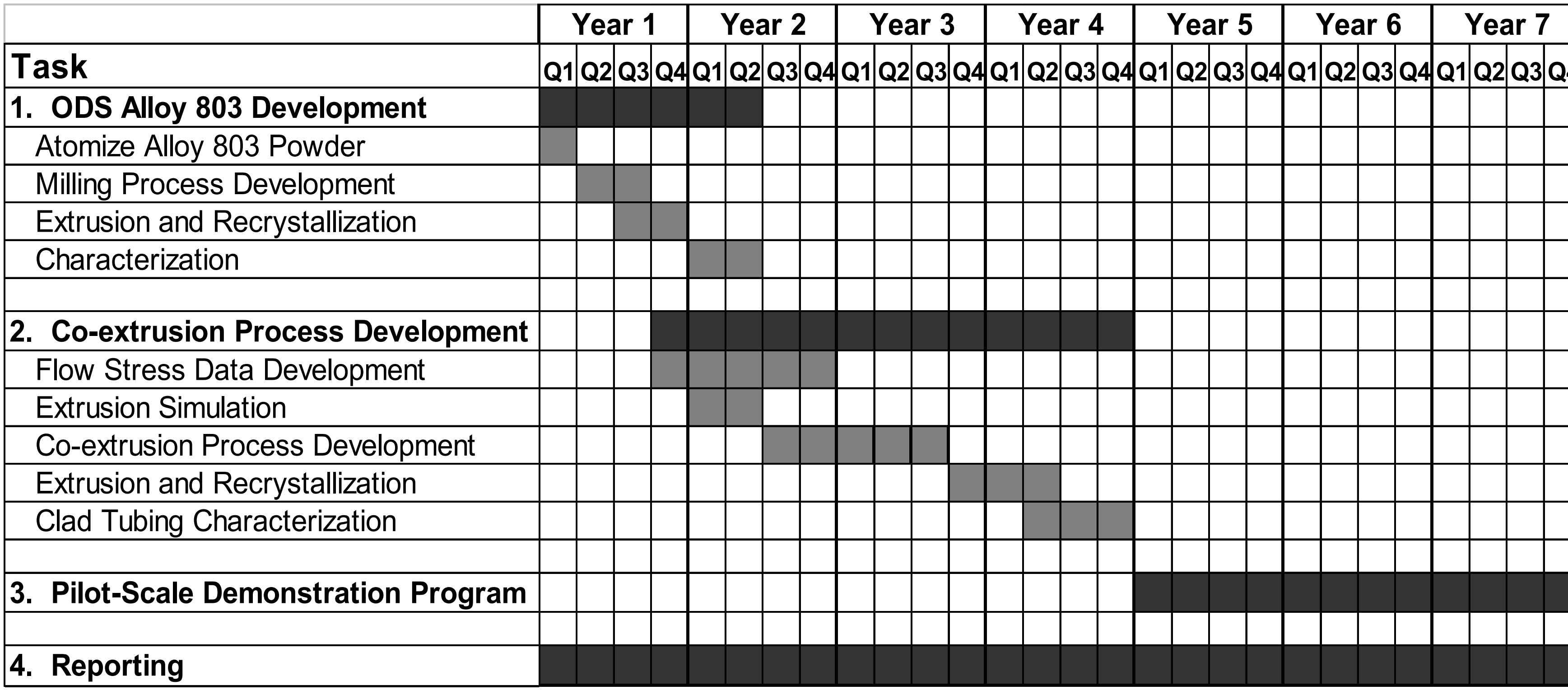
Project Schedule



Anticipated Spending Plan

Requested Funds	Task 1	Task 2	Task 3	Task 4	TOTAL
Year 1	133,527	40,700	0	30,729	204,956
Year 2	45,077	158,060	0	32,141	235,278
Year 3	0	207,416	0	33,628	241,044
Year 4	0	213,241	0	35,190	248,431
Year 5	0	0	188,379	30,666	219,045
Year 6	0	0	196,664	32,015	228,679
Year 7	0	0	205,358	33,430	238,788
TOTAL	178,604	619,417	590,401	227,799	1,616,221

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